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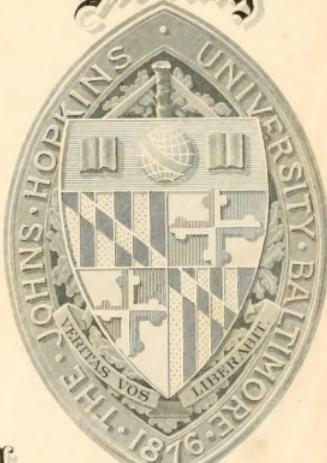


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JAH THESIS  
Parks,  
R. M.  
1892  
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On The Action  
of Methyl Alcohol  
on  
Para-Diazo-Ortho-Toluene  
Sulphonic Acid.

Dissertation

Presented for the Degree

Doctor of Philosophy

at the  
Johns Hopkins University

by  
R. M. Parks, Jr.  
1892

5-4 4141

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para-methoxy ortho-toluenesul-	
phenoxychloride	4%
para-methoxy ortho-toluenesul-	
phenoxy-imide	44.
<del>Combination of the methoxy for acetyl with phenylacetil with the symmetric sulfone-acid of Dimpfright and Weffler</del>	
para-methoxy benzoyl sulfone	47.
para-methoxy benzoyl sulfone	40.
Acid potassium salt of same	65.
para-methoxy ortho-substituted acid.	7%
Acid potassium salt of same	67.
Acid potassium salt of same	70.
butenyl (methyl) substituted	74.
Combination of para-methoxy ortho-	
sulfobutyl acetil with sulfo-	
acetic acid.	75.
Combination of phenylacetil	75.
Acetoacetic acid	77



~~Percent of methionine by weight, soluble  
inile volatile fatty acids~~ 71.  
Beta - hydroxyglutaric acid 70.  
Succinic acid 73.



## Acknowledgment.

The work described in this paper was carried on under historical botany of the Robbins University at the suggestion and under the scientific supervision of Professor Powers. I desire to record here my expression of gratitude for the instruction and advice received from him during my course at this university. I owe much also to the instruction received from Professor Morse in quantitative analysis and Professor Williams in mineralogy and geology.



## Introduction.

The investigation, of which one account is given here, was undertaken for the purpose of studying the decomposition of para-diazotetra-toluene sulphonic acid in methyl alcohol. A description of some transformations of the product of the reaction follows.

The decomposition of diazo compounds in different alcohols has been studied, as is known, in a large number of cases, since the first discovery of these compounds by Grignard in 1860. His results first reacted by Grignard led him to make the general statement that diazoic compounds are decomposed by boiling alcohol the vapour



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is eliminated and hydrogen takes its place, this so called triox or hydroxygen reaction suggested a convenient method for the replacement of the nitro group by hydroxyl.

This method however was not found to be applicable in all cases. Many experiments, notably among the first Nirobiansky, in attempting the replacement of the nitro or nitile group with hydroxyl, by converting into the corresponding compound decomposing it with ordinary reagents and thus forming compounds resulted instead of hydroxyl. The conditions which are favorable to the hydroxygen or hydroxy reaction have been studied recently



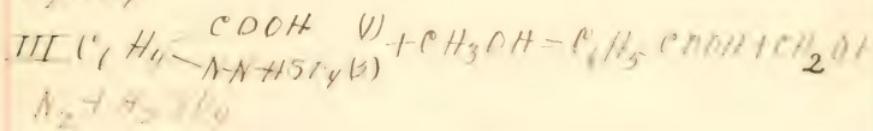
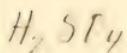
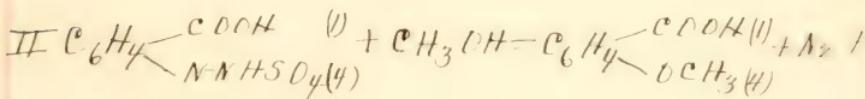
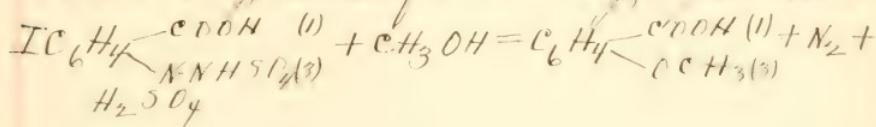
appeared. These investigations have led to interesting suggestions as to the influence of the position and presence of certain groups in the benzene nucleus, viz. the influence of the dilution of the reagent and pressure on the course of the reaction. The alcohol used generally in these experiments has been ethyl alcohol. Differences were found when some reagents were found to become prosed by different alcohols, as methyl, ethyl and propyl alcohols. It was also observed that because of the reaction between methyl alcohol and water was not very numerous.

It was also observed that amidine or amido-tri-methylbenzene was



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dearolized and decomposed with methyl, ethyl, and amyl alcohol were the corresponding ethers of the aromatic phenol. We also obtained diisopropyl  $C_6H_5COCH_3$  from benzene and isopropyl alcohol. It was mentioned in the product of the benzene,  $C_6H_5COOH$ , reacts with methyl alcohol. The nitro and para quaternary methoxy products, the ortho one being vicinal, according to the following equations.





Cruséau of this laboratory, in the same year 1861 had observed the formation of anisic acid according to equation II.

Two decompositions of anisic compound with methylalcohol with variation of pressure have been made, both in this laboratory. Metcalf<sup>7</sup> studied the decomposition of para-anisic or meta-aluminum substituted acid with methyl, ethyl and propyl alcohol. He draws two conclusions which have an important bearing on the course of the reaction; Increase of pressure and the simpler the alcohol, the greater the yield of alkene product.

Blecker<sup>7</sup> found that the time



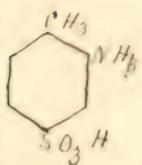
composed of one sulfonated and  
water-soluble acetate were only the  
hydrogen-bonded at least three  
times that of the pure ester. In some  
when mixed together in equimolar  
tobe only the melting product was  
formed.

The work of Helfand, Martin, Cahn  
and that of Kelen, László, and Imre Róna  
and Hirschfelder are the closest relatives  
to the investigation described in  
this paper.

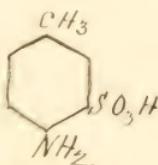
Now, take incense-burning thallic  
compounds of the type shown  
below and the acetate formed  
ordinarily by burning the incense  
and you get the smelting form  
sufficient acid, or no acid at all,  
edit. methyl cresols and phenol.



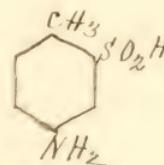
Hayduck and Hünfster found no difference between the diazo-compound obtained from the para-methoxy-ortho-toluenesulfonic acid and methylsulfuric acid obtained in the para-methoxy-ortho-toluene with oxalic acid, this acid is apparently identical with the acid obtained in this investigation. A comparison of the formulas of the amidosulfuric acid from which Hayduck's compounds were obtained are given here. The last one is the one used in this investigation.



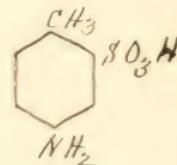
Hayduck



Metcalf



Hünfster

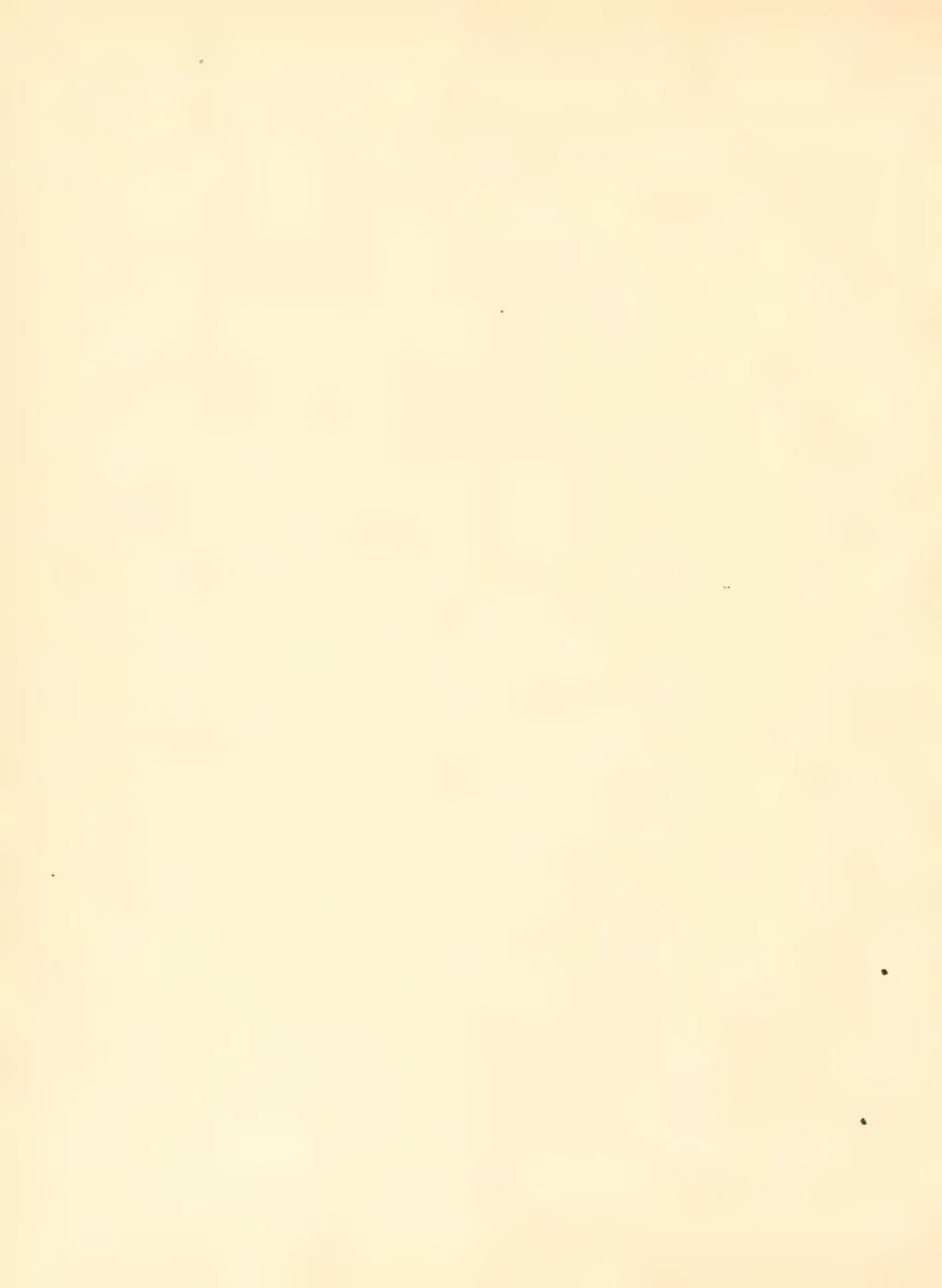




1.

Preparation of para-toluidine  
-o-sulphuric acid.

The starting point of the present investigation was para-nitro-  
toluene. This combined together  
with fuming sulphuric acid were  
used by Kuhns and Deissel  
for the purpose of preparing para-  
nitro-ortho-toluene-sulphuric acid.  
According to their directions one part  
of the para-toluene was treated  
with four parts of fuming sul-  
phuric acid. The flask containing  
the mixture was lowered into water  
which was then heated to boiling  
temperature of water for four  
to five hours. After cooling the  
darker viscous liquid was poured  
into twelve parts of cold water.



If an aqueous solution had not been  
boiled before by the sulphuric acid,  
this is filtered off, and after drying  
may be used again for the same ex-  
periment. If a sufficient amount to-  
gether with excess of sulphuric  
acid was then neutralized by  
chalk, filtered through a cloth fil-  
ter from the gypsum, which should  
be repeatedly washed with hot wa-  
ter, the filtrate containing the  
calcium salt of the sulphonic  
acid was again filtered. This time  
through filter, the calcium pre-  
cipitated by potassium car-  
bonate. The solution of the calcium  
was separated from the calcium  
carbonate by filtration and con-  
tinued to crystallization.



*Potassium salt* was obtained by passing a mixture of steam over a molten salt. This potassium salt was used for the reduction of the nitro group by tin and copper boride in caustic, according to the method described by Monk et al. and Reddish.

Five parts of the potassium salt, six parts of granulated tin, thirty parts of commercial mordanting acid, were gently heated until the reaction began, when the heat was turned off. The reaction proceeded vigorously, constantly throwing hot sulphuric acid off the reduction, which was over five minutes. According to the scale, salt of stannous boride and the mordant acid separated.

Yankee Henry Four. 9.399.



lattice mass. This was collected in a formless greenish grey by solution, dissolution in water and treated with a solution of sodium carbonate to precipitate the zinc and made the soluble sodium salt of zincumic acid.  
The following day the filtrate the zincumic acid was precipitated from its sodium salt by 10% potassium iodide. After dissolving in boiling water, heating until a uniform clear solution the acid was obtained in almost colorless rhomboidal crystals.  
A hard white ester between sulfuric acid is almost insoluble in cold water, difficultly so in hot water, insoluble in strong alcohol.



in the evolution of the drug or compound.  
All the various methods described  
in the literature for isolating  
amidocarboxylic acids that if suspended  
in a glass tube and treated with dilute  
ice water was used hence, adding  
nitrous fumes through this emulsion.  
However this does not affect the isomer  
ic compound ethyl tetrahydro, para  
sulphonic acid, but more the specific  
directions given by Lonsdale and  
de Rode<sup>1</sup> have recorded most authoritative  
ways. The first of these, living, living  
wide, with suspended ice over and  
over half part of water were shaken  
together cool with ice water and  
a rapid current of nitrous fumes  
produced by ammonium fluoride  
and nitric acid (ib. p. 2, p. 35) and



passed through it about fifteen  
minutes the reaction is over. The  
slag or compound was then washed  
with well cooled acid oil, filtered  
quickly with aid of the pump, and  
washed with oil, after which  
from the filter the slag or compound  
was spread upon burning paper.  
There the color of silver is no longer  
detectable the slag is ready for  
further use. In this manner as  
much as 120% of the amido acid were  
charred in fifteen minutes giving  
a yield of 40% by weight  
of the acid used. This slag com-  
bined is colorless when first made  
but soon becomes brownish. At ordinary  
air temperature it is stable for  
months if kept in vacuum.



for absolute alcohol, decomposes at 130° C. insoluble in chloroform, ether, soluble in water yielding boiling water form cresol and sulphuric acid.

Decomposition of the dicyclic compound with methyl alcohol.

It has already been stated in the introduction that dicyclic compounds in decomposing with alcohol, sometimes follow the first stage in which, sometimes the second stage reaction occurs both, I. e., if I had studied the reaction of this same dicyclic compound with ethyl alcohol under various conditions of pressure and heat found that both the hydrocarbon and oxygen containing compounds



were formed.

The isomeric ethylbenzenes, hence  
the meta toluenesulfonic acid  
have been studied by the author, with  
methyl, ethyl and propyl alcohols.  
Both the hydrogencation and dehydrogenation  
reactions resulted under pressure,  
in bulk with neither isomer,  
either the  $\alpha$ -para toluenesulfonic  
acid, obtained under the decomposi-  
tion decomposing at ordinary pres-  
sure with methyl and ethyl alcohols.  
A dehydrogenation reaction at ordinary  
pressure was made and it  
was found that the latter compound  
decomposed with the methyl alcohol.  
On evaporating the methyl alcohol  
a dark heavy liquid having an  
acid reaction remained.



acid was converted into the Borium salt by treatment with bare titanium carbonyle, and of adding the water solution, there would be isolated in tubular crystals together with a white powder. This result would indicate the formation of two products, namely the hydrogen and metallocy. This would be similar to the conduct of this latter with ethyl alcohol. This fact caused the first series of experiments to be made at ordinary pressure. These experiments were however according to the method pursued so successfully by Dusmill.

His method was to decompose the compound of the acid by collecting alcohol, in which the alcohol



neutralizing the resulting acids with barium carbonate and separating the nitrogen and chlorine products by repeated extraction with 5% percent boiling alcohol, for this may be calculated from the total barium salts, the specific weight of the barium chloride by alcohol, and if the residue, it was possible to calculate the percentages of the products formed. The extraction was based on the difference in solubility of the barium and chlorine salts in boiling alcohol. The chlorine compound being but slightly soluble.

In the first series therefore three experiments were made under like conditions i.e. at ordinary pressure



with absolute methyl alcohol. To indicate the progress of heating, compound was boiled with  $200^{\circ}\text{C}$  of absolute methyl alcohol in an Erlenmeyer flask connected with an inverted condenser. The composition of the liquid was observed when the boiling of the alcohol commenced, also indicated by the change of color of the liquid which was at first color of fresh cherry red, at the end of the decomposition reddish brown. The reaction was complete in about one hour and fifteen minutes. By this time all solid material had disappeared and formed an alcohol-soluble brownish-yellow product. The evolution of gas, carbon dioxide was then connected with another flask



chloroester and the chlorine distilled from the product of the decomposition. From the preliminary experiment the acid residue was converted into the barium salt by means of pure barium carbonate. The water solution of the barium salt was evaporated to dryness and dried in the air bath at 100°.

Experiment I	10 <sup>g</sup>	diso	gave	13.54 <sup>g</sup>	{
" II "	" "	" "	"	13.49	
" III "	" "	" "	"	13.51	

### Barium salt.

The three portions were again dissolved in water and evaporated to crystallisation. There first appeared a nearly white, not well crystallised salt, and then well crystallised yellowish-



combining redaction from tables  
it was stated above these were  
taken to be two different salts  
of barium. Attempts to separate  
them for analysis. The method  
by alcohol is described by Sie-  
gel. I did not prove satisfactory  
in order to get material for inter-  
mediate analysis the well crystal-  
lized portion was separated me-  
chanically from the white powder.  
The tubular crystals were first  
analyzed. The determination  
of the water of crystallization  
brought to light some inter-  
esting facts. The salt begins  
to lose water at  $60^{\circ}$ , at from  
 $110^{\circ}$  to  $150^{\circ}$  the weight is constant  
The loss in weight corresponds



closely to the loss of two molecules of water from the compound. On further heating to  $165^{\circ}$  the third and last molecule of water of crystallisation was driven off and higher heating did not produce any further loss, the analysis for water of crystallisation and barium gave the following results.

I  $0.0530$  gram of salt lost at  $165^{\circ}$   
 $0.0230$  gram of water and gave  
 $0.0910$  gram of barium sulphate

II  $0.0316$  gram of salt lost at  $165^{\circ}$

$0.0216$  gram of water and gave

$0.0937$  gram of barium sulphate.

Calculated for  $(C_6H_3-\overset{CH_3}{S}O_3)Ba\overset{CH_3}{O}3H_2O$

	Found	Calculated
$H_2O$	7.11	7.09
$Ba$	23.13	23.02



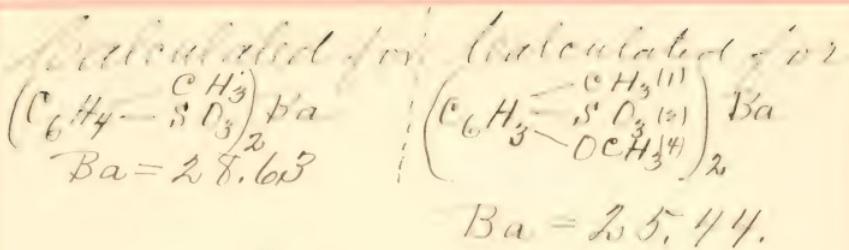
Estimations of barium were now made with both the two crystallised portions and also of the mixture of the well-crystallised and non-crystallised which could not be separated mechanically. In the case of the white powder or non-crystallised portion it was not possible to determine whether if crystallisation the results did not agree with each other. The analyses were made from the white powder and the mixture after volatilising at  $165^{\circ}$  and gave the following results.

I. 0% 060 gram of the powder gave 0.0792 gram of barium sulphate.  
II. 0% 377 gram of the mixed gave



0.1043 gram of barium sulphate.  
III 0.2086 gram of the mixture gave  
0.0896 gram of barium sulphate.  
IV. 0.2541 gram of the mixture gave  
0.1091 grams of barium sulphate.  
If the hydroxyl radical had  
taken place at all one would  
expect to find the barium salt  
of o-*ta*-toluene-sulphonie acid.  
The comparison of the four figures  
of barium in the above four analysis  
with the percentage of barium  
in barium o-*ta*-toluene sulphonate  
and in barium para-methoxy-ortho-  
toluene sulphonate, would give  
a strong indication as to the course  
of the reaction. The calculated  
percentage are for the sulphonate  
salts.





### Ground

I	II	III	IV
25.44	25.58	25.26	25.26

In these analyses there is no evidence that the hydrolysis reaction had taken place. If it had occurred at all it was in such small quantity as to escape detection by analysis. Further in collecting the gas given off during the decomposition no satisfactory evidence could be obtained of the presence of formaldehyde, i.e. the gas was nitrogen only. The different forms of



had been analysed for barium with the results studied above were changed into the sodium salt. This sodium salt treated with balsal for us benzoquinone. The acid obtained thus formed was tricarboxylic acid the amide formation of strong carbon ammonia. There resulted only one amide melting at 150°. In fact all the derivatives and transformations subsequently made lend additional evidence that there was only one product formed. This product at ordinary pressure is formed with 17% ortho-toluene sulphuric acid.



Experiment at increased pressure.  
In order to study the influence  
of pressure on the course of the re-  
action one experiment was made  
at an increased pressure of 2,000 mm.  
and one experiment at a diminished  
pressure.

The experiment at increased  
pressure was conducted in the  
apparatus used and described  
by Schner and others. This appa-  
ratus consists of a strong one  
and one-half liter balloon flask  
covered with a close net-work  
of copper wire (about one-quarter  
inch mesh). This flask was fitted  
with a two-hole stopper (rubber)  
which was bound down during  
the experiment. It too weighed



was fitted a bent glass tube connected with an open ended U-tube mercury manometer graduated in millimetres. Into the other hole through the stopper was fitted a copper tube, at the top of which was a conical valve provided with a lever on which it was hung a leaden weight. By adjusting this weight any desired pressure could be obtained.

Four grams of the diazo compound were decomposed with absolute methyl alcohol in the pressure flask at  $200^{\text{mm}}$  pressure. The same phenomena were observed as at ordinary pressure only the decomposition reacted in about forty-five minutes. The barom-



Salt made from the acid  
dissolved, appeared like salt formed  
from the product of decomposition  
at ordinary pressure. Crystallizes  
more readily if the barium salt  
is dry heated at  $165^{\circ}$  without  
being <sup>too</sup> hot to separate any portion.  
The results were as follows.

I 0.1870 gram of substance gave  
0.0809 gram of barium sulphate.

II 0.2153 gram of substance gave  
0.0928 gram of barium sulphate.

Calculated for      Found  
 $\left( \text{C}_6\text{H}_5-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}} \text{H}_3 \right)_2 \text{Ba}$

	I	II
--	---	----

$$\text{Ba} = 25.44 \quad 25.44. \quad 25.36.$$

The only product of the reaction  
is therefore a salt nothing between  
acid and base.



Experiment at diminished pressure.  
The experiment was also conducted  
at one-half atmospheric pressure.  
The apparatus consisted of passing  
one liter balloon flask fitted with  
a three hole rubber stopper, so one  
hole was about  $\frac{1}{4}$  in. dia. but a con-  
nected with a vacuum <sup>u</sup>, through  
the second ran a thermometer. The  
tube of an upright condenser pas-  
sed through the third hole into  
the upper end of the condenser and  
fastened by means of a one hole  
rubber stopper the short arm of  
a three bend glass tube, the long  
arm of which terminated a few  
millimeters below a two hole  
rubber stopper in a filtering  
flask. A test tube was placed



obliged within the flask the  
open end being immediately be-  
low around the end of the long  
arm if the tube connected with  
the condenser. This tube served to  
collect the methyl alcohol should  
any distil over during the experi-  
ment. Through the second hole of  
the stopper in the filtering flask  
passed a bent glass tube one  
end terminating in the bottom  
of the flask the other end connected  
with a Bunsen suction burn.

By this means if water should  
be drawn into the flask from the  
burn it would not interfere  
with the experiment and read-  
mitting air into the apparatus, the  
tube terminating in the other



would conduct the water off completely. The pressure inside of the apparatus was regulated by connecting a rubber tube to the side tube of the filtering flask and closing the rubber tube with a Mohr pinchcock. The pressure could then be regulated by hand. By carefully watching the vacuum gauge or the thermometer the pressure could be kept constant for any length of time without varying more than  $2^{\circ}\text{m}$  if pressure or  $2^{\circ}$  of temperature.

The diast compound and absolute methyl alcohol were introduced into the flask, the pump turned on and at one-half atmosphere the flask would



in a water bath. The decomposition proceeded much slower than in previous experiments. The methyl alcohol boiled at  $49^{\circ}$   $51^{\circ}$ , pressure near  $370^{\text{mm}}$ . One gram of silver <sup>compound</sup> required six and one-half hours for complete decomposition. The methyl alcohol was distilled from the product of decomposition, barium carbonate added, and the barium salt evaporated to dryness dehydrated and analyzed for barium with the following results.  
I 0'1538 gram of substance gave 0'0668 gram of barium sulphate.  
II 0'1933 gram of substance gave 0'0735 gram of barium sulphate.



Calculated for	Found
I	II
$\text{Ba} = 25.44$	25.55 25.41
$(\text{C}_6\text{H}_3-\overset{\text{CH}_3}{\underset{\text{OCH}_3}{\text{S}\text{O}_3}}\text{)}\text{Ba}$	

As in the cases with ordinary and increased pressure only one product could be obtained and this was the methoxy compound. Variation of the pressure does not change the course of the reaction.

### Para-methoxy-ortho-toluene-sulphonic acid.

In all subsequent experiments larger amounts of the diazo compounds were decomposed with methyl alcohol. One hundred grams of the diazo compound were decomposed with one



color if methyl alcohol, the product after distilling the methyl alcohol is a dark brown liquid easily soluble in alcohol and water. Made in large quantities it shows signs of crystallization after standing twenty-four hours. Set aside for several weeks it solidifies but not in well defined crystals. Boiling with animal charcoal does not entirely remove the color, after many attempts a small quantity of the acid was obtained in well defined rhomboidal plates of a yellowish brown color. Decomposes without melting. The acid purified as far as possible with animal charcoal or the acid colored from



The well crystallized barium salt was used for melting salts.

Melt of para-methoxy-ortho-toluene sulphonic acid.



Because of this salt have dried from water, the salt crystallizes from concentrated water solution in large monoclinic tabular crystals with three molecules of water.

Only the well crystallized is formed from the hot solution of thirty four parts of the salt in one hundred parts of water. If the concentration is more than this the salt is deposited from the hot solution.



the form of a white boulder which  
was found here without any record of  
any glaciation. Since the crystalline  
begin to lose water at  $60^{\circ}$  also  
by shrinking in the air at ordinary  
temperature, it appears that  
water boiling water at a cer-  
tain concentration has all lost  
some of its water if crystallization  
is probably two molecules.

The salt is easily soluble in wa-  
ter, difficultly soluble in alcohol.



Prepared from the decinone of the  
fusocid which finely powdered  
calcite exceedingly soluble in cold  
less so in alcohol. It occurs with



it forms a colorless columnar efflorescent  
brownish red crystal crystals.  
Analysis or calculation gives the  
following results.

I. 0.2175 g. gram of the salt lost 17.1%  
0.0383 g. gram of water and gave  
0.0736 g. gram of calcium sulphate.  
II. 0.2404 g. gram of the substance lost  
0.0335 g. gram of water and gave  
0.0617 g. gram of calcium sulphate.  
Calculated for  $\text{Ca}(\text{C}_6\text{H}_5-\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$

	I	II
$\text{H}_2\text{O}$	14.01	13.90
$\text{Ca}$	7.78	7.58

Magnesium salt  $(\text{C}_6\text{H}_5-\text{SO}_3)_2\text{Mg} \cdot 5\text{H}_2\text{O}$

Prepared by neutralization



fructose with formic acid  
carbonate, very soluble in water  
and alcohol, it once cooler it will  
crystallise in radial tufts of  
short slender prisms, formed  
entirely in volatile plates.

Analytical for  $\text{C}_6\text{H}_{12}\text{O}_6\text{MgCO}_3$   
the following results.

I. 10.3175 g. weight loss on ignition 19.1<sup>1</sup>

0.0545 g. weight of water added 0.0002

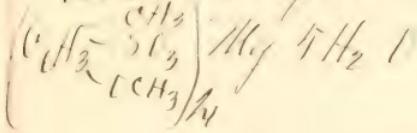
0.0767 g. weight of magnesium carbonate.

II. 0.2174 g. weight of substance lost

0.0376 g. weight of undissolved

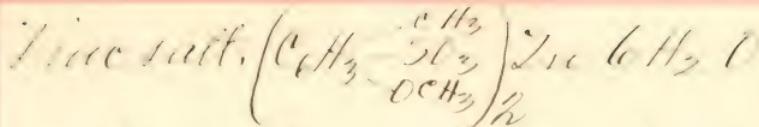
0.0495 g. weight of magnesium carbonate.

Calculated for  $\text{C}_6\text{H}_{12}\text{O}_6\text{MgCO}_3$



	I	II
$\text{H}_2\text{O}$	17.44.	17.07.
$\text{Mg}$	4.65.	4.81.



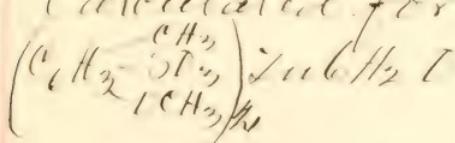


Prepared by neutralizing zinc  
chloride with zinc acetate and  
easily soluble in alcohol and water  
and crystallizes in short pointed prisms,  
dissolves forming water the fol-  
lowing results.

I 0.2441 gram of salt lost at 115°  
0.0466 gram of undissolved  
0.0344 gram of zinc oxide.

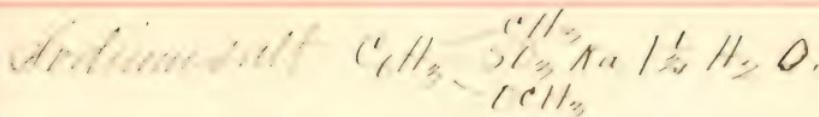
II 0.2791 gram of substance lost  
0.1541 gram of undissolved salt  
0.03674 gram of zinc oxide.

Calculated for 0.1 gram



	I	II
H <sub>2</sub> O	11.77	11.71
Zn	11.34	11.09

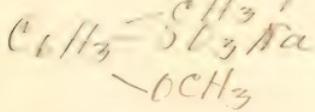




Prepared by slow precipitation  
of the metal from the aqueous salt  
with a solution of sodium carbonate.  
It becomes soluble in water and alcohol.  
When it is heated it melts before the  
solution in cooling solidifies into  
compact mass of almost colorless  
leaflets. Analyses gave the following:  
I. 0.2144 gram of salt lost at 161°  
0.0304 gram of water and gave  
0.1114 gram of sodium sulphate.

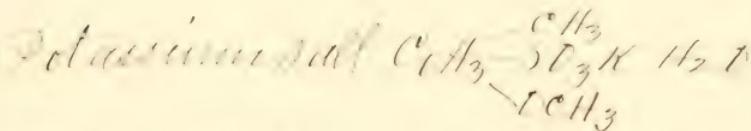
II. 0.2763 gram of substance lost  
0.0303 gram of water and gave  
0.0614 gram of sodium sulphate.

Calculated for  $\text{C}_6\text{H}_5-\overset{\text{C}_6\text{H}_5}{\text{Sb}_3}\text{Na}$





	I	II
Hg	10.75	10.69
Ni	9.11	9.25



Obtained by a cold precipitation  
 of the metal from the barium salt  
 by a solution of potassium carbo-  
 nate. Very soluble in water and  
 alcohol. From the hot concentrated  
 solution there is let aside a mass  
 of almost colorless fine branching  
 needles. Analysis gave the fol-  
 lowing results.

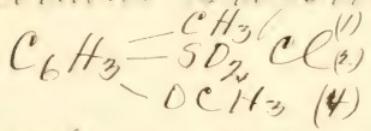
I. 0.2247 gram of the salt lost  
 0.0160 gram of water and gave  
 0.0771 gram of potassium carbonate.  
 II. 0.2319 gram of substance



0'0163 gram of benzene-methoxy  
0'0477 gram of barbituric acid.  
Calculated for Sodium  
 $C_6H_5\overset{CH_3}{S}O_3K H_2O$

$\text{OC}_2\text{H}_5$	I	II
$H_2O$ 6'77	6'77	7'74
K 15'11	15'07	15'04.

Chloride of benz-methoxy, titro  
volume barbituric acid.



The sodium salt was either  
by neutralising the free acid or  
with sodium carbonate or by  
precipitating the metal from  
the barium salt with a solution  
of sodium carbonate, was dried  
at 100°. The dried salt was



Mixed with a slight excess of nitro  
benzene as benzonitrile it distilled.  
The reaction was slow for a few minutes  
proceeded with violence and  
evolution of considerable heat.

Most of the black tars as organonitride  
was blown off by the heat of the  
reaction, the last portion of the  
organonitride held back in the bottom  
chloride could not be entirely remov-  
ed even when heated to  $140^{\circ}$ .

Upon cooling the acid chloride was  
poured into a large amount of  
cold water and washed.

The ester is a waxy oil yellow-  
ish white in color, very soluble in  
ether, from which it was not ob-  
tained crystalline but again became  
wax after evaporation of the ether.



After melting, or the solution will  
blow, while,  $\text{C}_6\text{H}_5\text{S}(\text{O}_2\text{NH}_2)\text{CH}_3$

Produced by treatment of the zinc iodide with strong aqueous ammonia. The reaction being violent, the excess ammonia soon became  
boiled vigorously, and after shaking  
for a short time the amide  
suddenly solidified into a very  
white mass. After evapora-  
ting off the excess of ammonia  
the water bath undecolorizing  
with sulfuric acid, the amide  
was filtered, washed with cold  
water. The amide is very soluble  
in alcohol, in which it is easily  
solved and colorless with no  
natural color. It is then



from the hot concentrated acetic acid solution as white plates. The amide is sufficiently soluble in cold and hot water. Upon boiling water it crystallizes in yellow needles if rapidly cooled, if slowly instead partially prisms with a vitreous center. Soluble in ammonia and in the alkaline carbonates from which it is precipitated on addition of acids. These are soluble without  $151^{\circ}$ . Mention has been made already that only one amide is formed from the product of the decomposition of the ester of ortho-methyl acetophenone.



Analysis for sulphur and nitrogen gave the following results

I 0.3471 g. of the sample gave  
1.4144 g. of barium sulphate.

II 0.3177 g. of the sample gave  
0.3721 g. of barium sulphate.

III and IV determinations for  
nitrogen after Kjeldahl.

Calculated for

	C <sub>6</sub> H <sub>3</sub> —S—NH <sub>2</sub> —OCH <sub>3</sub>	Found
S.	I	II
5.	15.94.	16.01. 16.09.
	III	IV
N.	6.98.	6.79. 6.90



Comparison with the only methyl  
toluenesulphonic acid of Siegfried  
and Steffter<sup>1</sup>

Differ in value studying benzene  
<sup>2</sup> & toluene with this sulphonic  
acid had a second time this sulphonic  
acid with the corresponding sul-  
phuric acid, we found that the  
acid amido or the toluenesulpho-  
nic acid and decomposing this  
compound in the volatile methylid-  
ene, he obtained a more volatile  
organic volatile acid called ex-  
methyl-toluene-sulphonic acid (and  
got a steep formulae  $\text{C}_6\text{H}_5-\text{SO}_3^{\text{H}}-\text{OCH}_3$ )

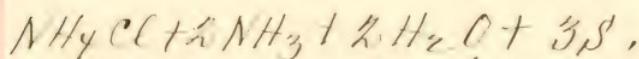
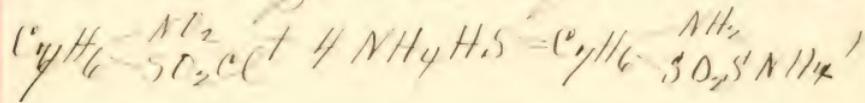
This acid is sufficiently similar  
with the product obtained under  
the investigation which however



either followed or preceded by a  
decomposed yellowish colour.  
At the latter stage it is yellow,  
its vitriocal and black streaks  
and molten parts are particularly  
well described by the  
yellowish base, covered with  
faint streaks of various tints.  
It was thought advisable to re-  
heat it in a furnace, so the fire  
was again kindled. The heat  
was soon sufficient to melt the  
metals and mix them with  
sulphuric acid. The  
violet of Heliotrope was  
lost by heating, but the  
blue flowers became more  
crystallized from their white  
heated and decomposed mass.



Substitution becomes very complete  
immediately after the amide  
with chlorine has been added,  
according to the equation.



After concentration of the liquid  
and removal of the separated  
sugar, the difficultly soluble  
free thiosubzonic acid is pre-  
cipitated by acetone.

This reaction was performed  
at room temperature and is descri-  
bed in a red yellowish brown.  
The colour of the thiosubzonic acid  
is effected by boiling with 10%  
trichloroacetic acid or by means  
of sodium methylate.



adviseable latter. Therefore dilution of most of the solution so that the sulphuric acid were removed by about 600 g. of sodium amalgam made by bringing together 60 g. of mercury and 20 g. of granulated metallic sodium. But this solution the mixture of the Hg & soap is changed to so. but one suboxide, dilution of acetic acid precipitated the sulphuric acid  $C_6H_5\frac{CH_3}{SO_2H}^{(1)}$ .  
 $NH_2(4)$

Recrystallized from hot water the acid was obtained in colorless hard prisms.

The diastereoisomer of the sulphuric acid was made by Heffter by fusing with



internally covered by soluble material  
in which the finely divided sulphuric acid was suspended. The  
latter concentrated forms yellow  
yellowish brown masses which are soon  
converted into a viscous lateral  
mass decomposing it at ordinary  
temperatures with separation of  
a brown resinous substance in oil  
color and ether. This last con-  
tinues until the decomposition  
considerably exceeds ordinary  
temperature and continues by  
removing ordinary pressure  
sure. No hydrolysis was observed.  
A clear alcoholic solution  
water was added and after fil-  
tering from the precipitated  
resin, evaporated and recrys-



obtained and passed into the  
various salt of zinc chlorothe  
toluenesulfonic acid. <sup>C<sub>11</sub>H<sub>12</sub></sup> 10.11  
<sup>C<sub>11</sub>H<sub>11</sub></sup> 10.15

~~Friedrich and Hoffer made in  
the work of research on the basis of  
of the same conditions the following sub-  
stic acid. This was a process I  
could not decompose well  
ethyl alcohol with carbonic  
gas at 300 mm when the  
same substance did not decompose.  
The difference in the amount of the  
two days compounds with  
alcohol and water exceed five  
hundred. Hoffer to make the  
statement that the two days  
compounds were not identical  
although they obtained by~~



from para toluidine substituted  
with identical substituents. Thus, for  
example, the para-toluidine obtained  
by decomposing the nitro-  
para-toluidine at increased pressure  
was substituted mainly in the ortho  
position, whereas the toluidine  
substituted obtained by them  
was identical with that of Sim-  
bolit and Hoffler. The latter thinks  
thus on not the same, because the  
substituents, respectively, Simbolit  
and Hoffler give the melting-point  
at  $136^{\circ}$ , whereas  $143^{\circ}$  to  $144^{\circ}$ . The  
substituted has been obtained in  
considerable quantity and in a  
very pure condition by Döller.

Yours sincerely & truly  
Hans Döller



and afterwards by Swett and  
Foster in the melting point at  
 $143^{\circ}$   $144^{\circ}$  which is undoubtedly  
correct.

There are also differences which  
exist in the descriptions given by  
Gmelin and Raffler for pure  
nitrous or the benzene sulfonic  
acid, its barium potassium  
salts and the description given  
in his thesis. They describe the  
acid as non crystallizing giving  
a barium salt which decomposes  
by evaporation of its water solution  
and becomes strong  
odor of creosol, and without con-  
stant composition. The fuming  
viscous yellowish oil, melting  
at  $55^{\circ}$ .



In this work the acid was obtained in well defined crystals the barium salt well crystallized and of constant composition and without color if resolved on boiling the water solution of the salt.

The descriptions of the barium and amide agree closely.

In making the barium salt by titration with toluene sulphuric acid according to the method of Langrisch and Seffler the colourless products were found to correspond with their description. The salt of the sulphuric acid was suspended in absolute methyl alcohol, well cooled and nitric fumes passed through it. The salt <sup>completely</sup> dissolved and just short twice its own weight then recrystallized.



filtered and washed a few times  
with ~~absolute~~ <sup>90%</sup> alcohol. The last  
washings placed in a flask were  
~~mixed~~ <sup>90%</sup> alcohol; heating was  
continued at ordinary temperature  
and by warming till the water bath  
was over its highest time. Water  
was added, the precipitated mass  
filtered off, and the filtrate evap-  
orated in the water bath. Benzoic  
carbonate was then added, the  
barium salt filtered from the  
~~aggregates~~ <sup>barium carbonate</sup> and  
dried <sup>over</sup> calcium cyanide, after  
being heated in salt; was dis-  
solved in absolute alcohol by  
boiling. After cooling addition  
of ether precipitated the salt as  
a yellowish powder as shown



it by Höffler, so far the work  
of Hippel was repeated.

Efforts were now made to obtain  
the salt in crystallized form, by evap-  
orating from water. The experience  
obtained by working with large  
quantities of the barium salt of the  
methylene acid, had indicated the best  
method to pursue, now if it were  
possible to obtain from water  
solution crystals of the barium  
salt obtained by the method of  
Guinier and Höffler, like the  
crystals of the barium salt of the  
methylene sulfonic acid  
obtained by the decomposition  
of the clear or para-imido-ortho  
toluenesulfonic acid in methyl  
alcohol strong water could



resulted of furnished of the solubility of the two products. When  
the barium salt was the only product isolated by this process,  
it was dissolved in water and  
boiled with animal charcoal.  
After filtering, the solution of the  
salt was left until it had  
its crystallization. According to the  
concentrated solution therefore ob-  
tained a white powder then well  
defined crystals like the barium  
salt described at the beginning  
of this paper. The yield of barium  
salt was very small, twelve grams  
of the seed being acid giving but  
little more than a gram of the  
barium salt if the mallow acid  
is off used.



of the sulphuric acid gave a volume  
equal to the free barium salt of  
the electrolyzed solution the yield of  
the methoxy salt was still smaller.

100 cc. of water were measured  
and the following results,  
I 0.2588 gram of the salt lost.

0.2332 gram of water remaining  
0.1036 gram of barium sulphate.

II 0.25734 gram of salt & when  
dehydrated at 165° 0.1202 gram  
of barium sulphate.

Calculated for Ba<sub>3</sub>H<sub>2</sub>O  
 $\left( \text{C}_6\text{H}_5-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}_6\text{H}_5}} \right) \text{Ba}_3\text{H}_2\text{O}$

I

H<sub>2</sub>O 9.11. 8.96

Ba<sub>2</sub>H<sub>3</sub>.13. 23.55

Calculated for dehydrated salt

Ba<sub>2</sub>H<sub>5</sub>.44. 25.77 25.79



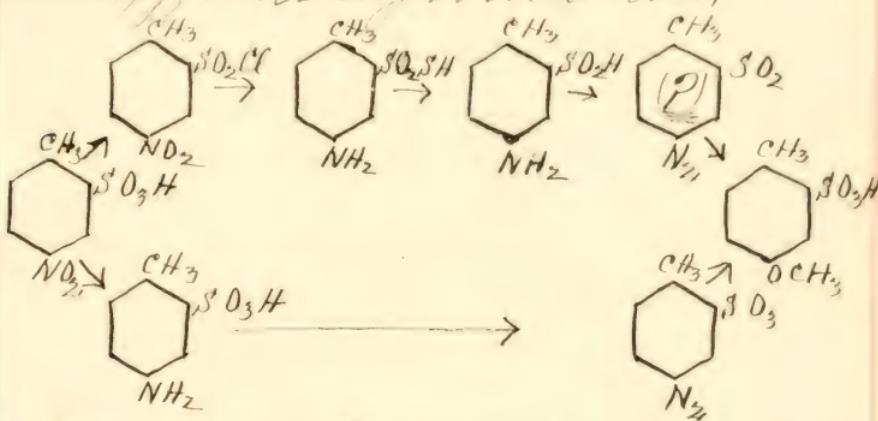
The difference was never examined down to the crystallizing power of the acid. But it must be said that only when working with large quantities of the acid is it possible to detect any signs of crystallization in its liquid state. But Hoffer worked only with very small quantity of the acid; it is not surprising that it was not obtained crystallized. The conclusion seems to be justified that the two natural acids are identical. Whether the large compounds from which the acids are derived are identical or not is a question to which no answer is not attempted at this time.

A comparison of the two methods starting from the same sulfurous acid and meeting again in the



6

Methionylic acid is given below,



To obtain the methionylic acid a very short study of the two transformations by the two methods would soon convince one which is the better one to follow. The method described in this paper gives large and very satisfactory yields at every stage from the nitration to the methionylic acid.



Action of ammonia on ortho-toluenesulphonamide.

Carried out by oxidising  
ortho-toluene-sulphonamide with  
potassium permanganate obtained  
the first member of a class of bodies  
of which was given the name of "sulphamide". Since this  
discovery, other members of this  
class have become known. The  
directions given in the first article  
for the preparation of benzene-  
sulphamide or "succinamide" were  
followed. 10 grams of para-methoxy-  
ortho-toluene-sulphonamide  
4 grams of potassium permanganate  
and water free of heat were  
placed in a covered vessel.

Yield 1.456



liter flask stood in water and  
heated for some hours at the boiling  
temperature of water. The color of the  
benzene solution disappeared in  
about three hours. The solution was  
then filtered from the insoluble  
manganese compound and  
concentrated to a small volume.  
Addition of hydrochloric acid pro-  
duced a white precipitate of fine  
needles. After filtering and wash-  
ing the precipitate in cold water  
it was dissolved in boiling cold  
alcohol. The compound is easily  
soluble in hot alcohol, difficultly  
in cold. May extract it on one  
side it thus easily separated as  
it is quite soluble in cold alcohol.  
From alcohol the yellow bar-



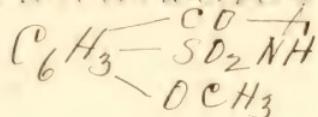
greenish white crystalline  
fragile long blade like crystals.  
It is sufficiently soluble in boiling  
water, according to my slender  
means, four to six centimeters in  
length appear. The crystals melt  
at  $257^{\circ}$ .

Analyses for sulphur and nitrogen  
show this compound to be para  
nitroxy benzoic sulphonate. The  
following results of analysis

- I. 0'1654 gram of the substance gave  
0'1706 gram of barium sulphate  
II 0'1733 g. of substance gave  
0'2025 gram of barium sulphate  
III and IV determinations for  
nitrogen after Kjeldahl  
(burning wood gasation)



Calculated for



S 15.04

N 6.59

Found

15.00—15.18

6.44—6.74

Sodium salt of methionyl bar-  
yric sulfonide ( $\text{C}_6\text{H}_3-\overset{\text{CO}^-}{\underset{\text{OCH}_3}{\text{S}\text{O}_2\text{Na}^+}}\text{Ba}(\text{OH})_2\text{O}$ )

Two grams of methionyl baryric  
sulfonide were dissolved in  
boiling water and pure barium  
carbonate added. After boiling  
sometime the excess of barium  
carbonate was filtered off and  
the filtrate evaporated to a small  
volume. The salt is easily solu-  
ble in water from which it



crystallizes in long colorless and  
also concentrically arranged.

The air dried salt was washed  
with absolute alcohol, recrystallized  
from water and analyzed for  
water of crystallization and bar-  
ium with the following result.

I 0.2437 gram of the salt lost

0.0215 gram of water and gave

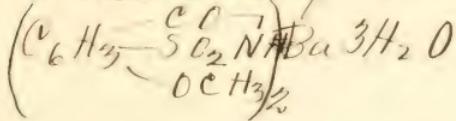
0.0980 gram of barium sulphate.

II 0.1160 gram of substance lost

0.0166 gram of water and gave

0.0701 gram of barium sulphate.

Calculated for  $\text{C}_6\text{H}_5\text{CO}_2\text{NBBa}_3\text{H}_2\text{O}$



I

II

$\text{H}_2\text{O}$  8.78. 8.82 - 8.92.

$\text{Ba}_2\text{H}_2\text{N}_2\text{O}_2\text{C}_6\text{H}_5\text{CO}_2$  19 - 22.17



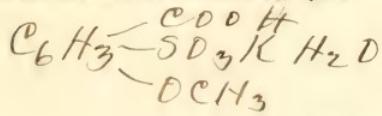
The filtrate from mellopp,  
barroic sulphuric bar. evaporated  
almost to dryness potassium  
chloride first crystallises there-  
long beautiful prisms almost  
colorless, which proved to be  
the acid potassium salt of para-  
mellopp or the sulpho barroic acid.  
This salt can be obtained from  
these mother liquors either by  
fractional crystallisation before  
it from potassium chloride or  
evaporation to dryness and ex-  
tracting with alcohol. The salt is  
much more soluble in alcohol



From potassium chlorate, and  
may thus be obtained by a  
hydrolysis of the salt gave the  
following results.

I 0.2628 gram of the salt lost 0.05  
0.0166 gram of water and gave  
0.0771 gram of potassium sulphate  
II 0.2224 gram of substance dehydrat-  
ed at 125° gave 0.0714 gram  
of potassium sulphate.

Calculated for Found



H <sub>2</sub> 0.6.7.5	6.3%
K 13.58	13.43

Calculated for dehydrated salt.

	Found
K = 14.44	14.44

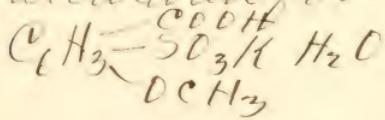


The acid potassium salt was made out by oxidizing the potassium salt of para-methoxy or the ferrocene-sulfonic acid. 10 g. of this salt were dissolved in one liter of water, 15 g. of potassium bromate added, and boiled in boiling water. The color of the ferrocene oxide disappeared in about two hours. After removing the insoluble manganese compounds evaporating to a small volume, strong hydrochloric acid threw down the acid potassium methoxy sulfobenzoate as short needles. These needles recrystallized from water and decolorized gave the following results.  
10% of guncotton



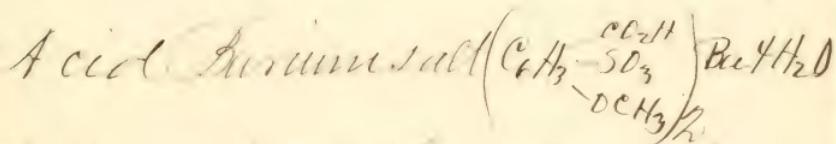
0'0174 gram of water soluble  
 0'0842 gram of potassium sulphate  
 II 0'2763 gram of the dehydrated  
 salt gave 0'0849 gram of pot-  
 assium sulphate.

Calculated for      Found



	I	II
H <sub>2</sub> O	6.25	6.29
K	13.57	13.66

Dehydrated K 14.44      14.99



Prepared from the free malic acid, a water solution of the acid was divided into two equal parts, one part neutralised with barium carbonate

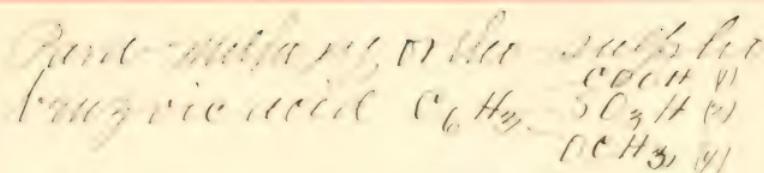


To this neutral barium salt the second part of the acid was added to produce the acid salt. Both the neutral and acid salts are extremely soluble in water and can not be obtained in crystals. I add hydrochloric acid. The acid barium salt is slightly soluble, from which it crystallizes in fine white needles, giving the following result.

0'2212 gram of the substance lost 0'0234 gram of water at 180° and gave 0'0761 gram of barium sulphate.

Calculated for	Found
$(C_6H_3-\overset{CO_2H}{S}O_3)Ba \cdot 4H_2O$	
$(C_6H_3-\overset{CO_2H}{S}O_3)Ba \cdot 4H_2O$	1
H <sub>2</sub> O 10'7%	10'3-8
Ba 20'44	20'24





This acid was first prepared from the acid potassium salt by heating with  $\text{NaCl}$  until the chloride was formed, then decomposing the acid chloride in boiling water, evaporating, drying, and recrystallizing from water. A second method is to pass from the methyl benzene sulphide to the acid. This is accomplished by adding the methyl, benzene sulphide in large quantity to the acid, one part of the concentrated acid to eight parts of water. In the case of the ammonium salt of the acid ammonium salt of the acid



suspending acid is formed.  
This acid combines with a salt when  
treated with twice its weight of  
phosphorus pentachloride gives the  
chloride, then this chloride is boil-  
ed with water and hydrochloric acid  
is given off and the acid is formed.  
It crystallizes from water so white  
it is quite soluble this acid appears  
as long interlacing needles, turns  
purple and colorless. It melts  
without decomposing at 104°  
on cooling it quickly solidifies  
and again becomes melted at the  
same point, this may be repeated  
without change of the melting  
point.

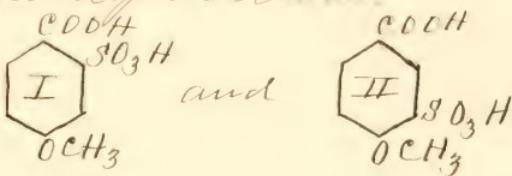


chloride of benzyl methyl for the  
 sulphobenzoyl chloride  $C_6H_5SO_2Cl$   
 $\text{OC}_6H_5$

The chloride prepared as above  
 described for the preparation  
 of the methylsulphobenzoyl chloride  
 was white solid, It does not  
 dissolve easily in ether from which  
 it crystallizes in small hard  
 crystals transparent and colorless.  
 The crystals powdered and boiled  
 with aqueous ammonia give the meth  
 ylsulphobenzoyl chloride melting at  
 71°.



Preparation of benzene rings  
with sulphuric acid with  
the sulphuric acid of Terao et al.  
Anilic acid  $\text{C}_6\text{H}_4-\overset{\text{COOH}}{\underset{\text{OCH}_3}{\text{S}(\text{O})_2\text{H}}}$  according  
to theory should give two sulphonic  
acids, one in which the sulphuric  
acid group would be in the ortho  
position to carbonyl the other  
in the meta position.



By derivation the acid described  
in this paper should be the one  
expressed by formula I.

It was thought advisable to repeat the experiments of Terao et al.  
follows; 3 grams of crystallized  
anilic acid were sulfonated



flask were covered with fuming sulphuric acid and heated in a water bath for two hours. After cooling the contents of the flask were poured into cold water. This solution of sulphuric acid and the excess of sulphuric acid was neutralized with an excess of lead carbonate. The lead sulphate was filtered off and repeatedly washed with hot water. The lead salt as described by Iowa was found to crystallize from hot water in beautiful transparent crystals. This lead salt was transformed into the sodium salt by precipitation of the metal with a solution of sodium carbonate. A portion of this salt was



in a silver crucible with potassium bichromate. The fused mass was dissolved in water and acidified with hydrochloric acid. Sulfur liquid was given off. The solution was extracted with ether. After evaporating the ether there appeared needles of protocatonic acid. A portion of the crystals was dissolved in water and this solution gave the characteristic color reaction with ferric chloride namely dark green. Addition of a very little sodium carbonate changed the green color blue passing rapidly into red. The melting point of the needles from ether was found to be  $194^{\circ}$ .  
The melting point of protocatonic



acid is variously given by different observers. Malicet who first made this experiment with sulfamic acid, gave  $199^{\circ}$  as the melting point. Barth and Schmitt<sup>24</sup> gave the melting point of pure bromo-technic acid as  $194^{\circ}$  (uncorr.). The melting point here found as is apparent agrees with that given by Barth and Schmitt.

In the same manner two grams of melting bromic sulfimide were fused with one gram of potassium bromide, the fused mass dissolved in water neutralized and extracted with ether. The crystals obtained after evaporation of the ether, dissolved in water gave



a purple coloration with ferric chloride. The temperature of the fusion with potassium hydroxide was not determined unless ~~unless~~ by infusing 1,2,4, 8 disulphobenzoic acid with potassium hydroxide and observed that at temperatures above  $250^{\circ}$  only resorcin is formed, below  $250^{\circ}$  1,2,4 dioxy benzoic acid together usually with a small quantity of resorcin. It was thought that the purple color resulted from the blue color given by resorcin and the dark-red color of 1,2,4 dioxybenzoic acid. This conclusion proved correct. To the solution giving the purple coloration sodium carbonate was added, ethylamine

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extracted with ether, which  
gave the characteristic blue colour  
when treated with ferric chloride and  
melted at  $104^{\circ}$ - $107^{\circ}$ .

The solution from which the  
resorcinol had been removed  
was acidified and extracted  
with ether. After evaporation of  
the ether, fine white needles were  
left behind. A solution of these  
needles gave a dark red coloration  
with ferric chloride characteristic  
of 1,3,4-tricyclic organic acid.

This acid is best described in  
chemical literature as resor-  
cylic acid. The melting point  
from ether melted at  $212^{\circ}$  to  $213^{\circ}$ .  
This melting point agrees well with  
that ascribed to resorcylic



acid by Pistorzycki and Post-  
mekoff. Two writers in their ac-  
count of the formation of 3 resorci-  
lic acid from resorcin by heating  
with potassium bicarbonate state  
that on heating rapidly the cul-  
tious acid melts at  $213^{\circ}$ . This  
statement is confirmed. Other  
writers give a different figure  
Blomstrand  $194^{\circ}$  Goldberg  $194^{\circ}$   
Benedikt and Hazewinkel  $147^{\circ}$   
Seeliger and Brauner  $194^{\circ}$   $200^{\circ}$   
Vilimann and Perrissine  $204^{\circ}$   $206^{\circ}$   
The products of the fusion of  
methylene benzoyl sulphuric with  
potassium hydroxide therefore  
are resorcin and 3, resorcylic acid  
while sulphamic acid gives  
phthalocetonic acid.

// Benckle 18-1985



by a process by formic acid (p. 75)  
The active blue shade of sulphuric  
acid would be para-methoxy,  
methyl sulphobenzoic acid.



### Summary.

I. When para-sulfioxy-toluene sulfonic acid is decomposed with absolute methyl alcohol at ordinary, increased, or diminished pressure only the methoxy product is formed namely, para-methoxy, ortho-toluene-sulfonic acid.

If this result does not conform to the rules deduced from the study of the decomposition of diazo compounds with ethyl alcohol but does confirm the suggestion that the simpler electropositive group is introduced more easily than the more complex ones.

III. The product of the reaction is identical with the ortho-methyl tol uene sulfonic acid obtained



I. Sulphuric acid is formed by the  
combustion of the zinc compound  
from para-anisole or the toluene  
sulphonic acid with methyl alcohol.  
IV When para-methoxyaniline toluene  
sulphonate is oxidized with  
potassium permanganate para-  
methoxy ~~sulphobenzoic~~ sulphonic acid  
is formed. From this can be ob-  
tained para-methoxy or the sulphonato  
benzoic acid.

V. Para-methoxy or the sulphuric  
acid is isomeric with sulpho-  
anisic acid and by fusion with  
potassium hydroxide, resorcin  
and  $\beta$ -naphthoic acid are formed.



## Note.

I The temperatures given in this dissertation will all be corrected.

If the atomic weights used in the calculations of this work was follows.

Ba	136.4	S	31.47
Ca	39.91	O	15.96
Mg	23.94	H	1.
Zn	65.1	N	14.01
Na	23.	C	11.97
K	39.03		



## Biographical Sketch.

The author of this dissertation, Albert Miller Banks Jr., was born at Bedford Indiana July 25, 1851. He obtained his college education at the University of Frankford Ind. In 1875 he entered Indiana University and graduated in 1879 with the degree of Bachelor of Arts. Six years were spent in teaching four of which was as teacher with natural sciences in college side institutions. Advanced courses of study were pursued by annual Howard University, D. C. and the University of Munich Germany, 1883. These years were a valuable & fruitful at the Johns Hopkins University while pursuing the principal subjects of mineralogy and geology, also a subordinate











